A Review on Natural Fibre Based Composites–Part I: Structure, Processing and Properties of Vegetable Fibres

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ABSTRACT. Natural fibre-based composites have been intensely studied in the last years due to their specific properties and their clearly positive environmental impact. Other advantages of using vegetable fibres are related to their economical production and processing, their safe handling and working conditions. Therefore, lignocellulosic natural fibres constitute an interesting alternative to traditional synthetic fibres in composite materials. This work is intended to present an overview of the main results presented in literature on this topic, focusing the attention on the fibres properties in terms of physical and chemical structure, thermal and mechanical properties. Some aspects related to the production of vegetable fibres for composites are also presented. *[Article copies available for a fee from The Haworth Document Delivery Service: 1-800-HAWORTH. E-mail address: <docdelivery@haworthpress.com> Website: <http://www.HaworthPress.com> © 2004 by The Haworth Press, Inc. All rights reserved.]*

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Part of the presented results has been obtained in the research work of the ECOFINA Project, in the framework of the 5th European Research Program. We would like to thank all the partner of the Project for the useful researches, and the other colleagues that have kindly furnished their contributes.

Journal of Natural Fibers, Vol. 1(2) 2004
http://www.haworthpress.com/web/JSF

Digital Object Identifier: 10.1300/J395v01n02_04

KEYWORDS. Natural fibres, cellulose fibres, fibre processing, retting, steam explosion, mechanical properties, thermal properties, composites

INTRODUCTION

After decades of high-tech development of artificial fibres such as carbon, aramid and glass, it is remarkable that natural fibres such as kenaf, flax, jute, hemp and sisal are still attracting renewed interest (English, Youngquist and Krzysik 1994; Bledzki and Gassan 1999; Nabi Saheb and Jog 1999; Eichhorn et al. 2001; Mohanty, Misra and Drzal 2002). In Figure 1 is shown the increasing trend of the production of fibre crops in the world for all industrial applications along the last forty years.

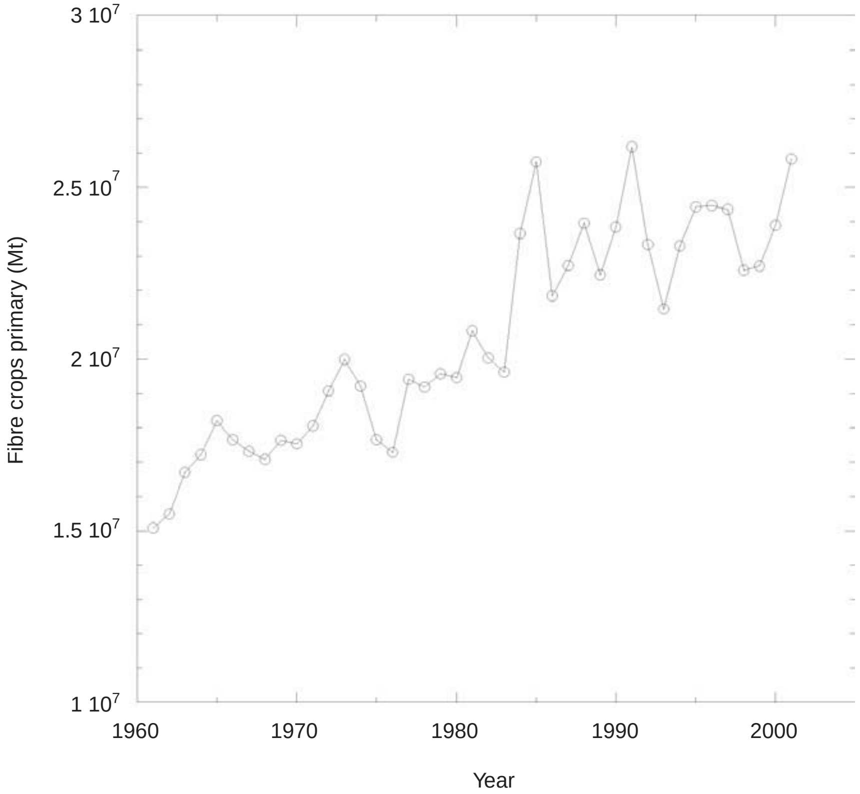
The main advantages of using natural reinforcements in composite materials, if compared with conventional synthetic fibres, can be summarized in the following (Brower 2000; Peijs 2000):

- biodegradability, therefore they can be eliminated from the environment after the life cycle;
- they can also be incinerated with energy recovery;
- lower specific weight which results in a higher specific strength and stiffness than glass;
- renewable resource, so the production thereof requires little energy; CO_2 is used while oxygen is given back to the environment;
- produced with low investment at a low cost which makes the material an interesting product for low-wage countries;
- friendly processing with reduced wearing on tools;
- better working conditions and no skin irritation;
- good thermal and acoustic insulating properties.

On the other hand, some disadvantages may limit their application on an industrial level:

- variable quality depending on several factors including unpredictable influences, such as weather;
- moisture absorption which causes swelling of the fibres;
- limited maximum processing temperature;
- lower strength properties, in particular, impact strength;
- lower durability but fibre treatments can improve this considerably;
- poor fire resistance;
- prices may fluctuate according to harvest results or agricultural politics.

FIGURE 1. Global fibre crops primary among the last forty years.

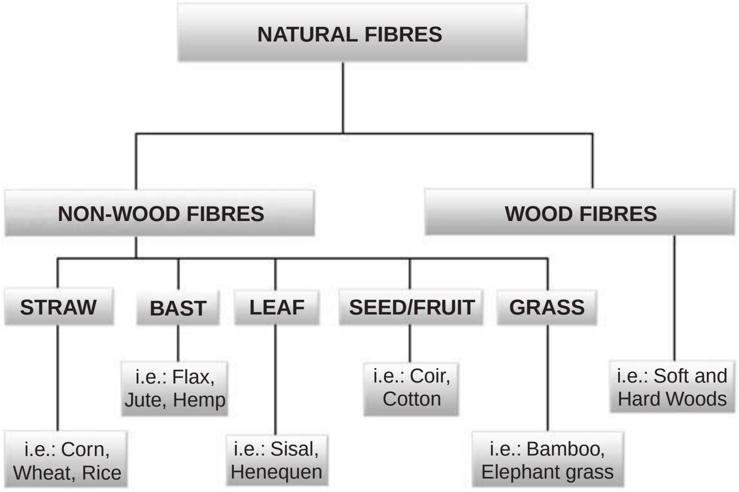


Most of the available information published over the last few years on natural fibre/wood composites dealt with several topics like identification and classification of fibres, treatments and adaptation of natural fibres, study of compatibility between fibre and matrix in composites, determination of fibre and composite mechanical properties, humidity effects and, finally, potential applications as substitutes for other materials. However, more extensive research is necessary to assess the standard quality of the fibres that is a function of raw material optimisation, growth-maturity-retting-decortication processes and the use of advanced methods for the preparation and processing of fibres. Moreover, in the case of their utilization as reinforcements in composite technology, it is also fundamental to improve the compatibility between the (hydrophobic-thermoplastic or hydrophilic-thermoset) matrix and the hydrophilic cellulose-based natural fibres (Rowell 1995; George, Sreekala and Thomas

2001; Joseph et al. 1996). The purpose of composite materials development is, in fact, to obtain a product able to combine the positive properties of each constituent component. In this sense, lignocellulosic reinforcements have been of growing interest in the last few years due to their environmentally friendly aspect (Rowell 1998). In fact, environment legislation as well as consumer demands are all increasing the manufacturing requirements of these materials and final products to consider the virtual impact of the products at all stages of their life cycle. The latter aspect validates the renewed interest that natural reinforcements have gained, especially as a glass fibre substitute in the automotive industries (Brouwer 2000, Kenny 2001). Furthermore, the development of specific manufacturing technologies has to be addressed in order to obtain reliable products based on these materials.

Natural bio-based fibres may be classified in two main categories: non-wood fibres and wood fibres (see Figure 2). Even so, the basic chemical structures of these kinds of fibres are similar in terms of the constituents varying their composition fibre-to-fibre (Mohanty, Misra and Drzal 2002). Most natural leaf, bast and seed fibres are actually used as reinforcements in the composite industry. Bast fibres (flax, jute, hemp) are typically the bests for improvements in tensile and bending strength and modulus. Instead, coarse fibres such as sisal and coir (coconut husk fibre) are better for toughness. In addition, other kinds of fibres and fillers, obtained from the processing of wood, coir, agave, hemp, jute, etc. as well as rice and nut hulls, cereal straws (oat, rye,

FIGURE 2. Classification of natural fibres.



wheat, etc.) and corn cobs can be used to improve dimensional stability and stiffness.

The objective of this first part is to introduce the main aspects of vegetable fibres used for composite materials by means of a general overview of the results presented in literature concerning this new typology of reinforcements, focusing the attention on the fibre properties in terms of chemical and physical structure, and on their thermal and mechanical characteristics. The second parting will be devoted to the final utilization of vegetable fibres as reinforcement of polymeric matrices (thermoplastics, thermosets and biodegradables), and to the review the most used methods for the improvement of fibre-matrix compatibility (physical and chemical treatments) with particular attention to the application of natural fibre composites in the automotive industry.

NATURAL CELLULOSIC FIBRES

Chemistry

Cellulose based fillers are simple materials, both chemically and physically. If one ignores the absorbed water, the main constituents of cellulose-based reinforcements consist of three types of chemicals: approximately half thereof is cellulose and approximately a quarter thereof is hemicellulose and lignin. Other extractives present in plant-sources include pectin and waxes (Hon 1991; Bledski and Gassan 1996). The compositions of some plant-fibres are shown in Table A.

Cellulose

The existence of cellulose as a common material in plant cell walls was first discovered by Anselm Payen in 1838 (Payen 1838a, 1838b). A natural polymer consisting of D-glucose ($C_6H_{12}O_6$) monomer units, cellulose contains glucose units which link together to form long unbranched chains. A schematisation of cellulose structure is reported in Figure 3 (Nevell and Zeronian 1985). There are roughly 4,000 to 8,000 glucose molecules strung together. The polymer chains in cellulose have a linear structure due to the 1,4-b glycosidic linkages. The repeating unit in cellulose is actually made up of two glucose units with each glucose unit in the linear chain being “turned over” when compared with its preceding unit. Due to the positioning of the three hydroxyl groups in each glucose monomer, strong hydrogen bonds are formed between these groups and the hydroxyl groups on adjacent chains. Cellulose is largely crystalline, organised into microfibrils and is very stable in normal environments. The H-bonding of many cellulose molecules to each other results in the formation of microfibres that can interact to form fibres. Cellulose fibres

TABLE A. Chemical composition of some vegetable fibres.

Fibre	**Latin name**	**Cellulose** (wt.%)	**Hemi-cellulose** (wt.%)	**Lignin** (wt.%)	**Pectin** (wt.%)	**References***
Flax	*Linum usitatissimum*	60-81	14-18.6	2-3	1.8-2.3	1
Jute	*Corchorus capsularis*, *C. olitorius*	51-72	12-20.4	5-13	0.2	2
Abaca	*Musa textilis*	60.8-64	21	12	0.8	3
Sisal	*Agave sisalana Perrine*	43-88	10-13	4-12	0.8-2	4
Kenaf	*Hibiscus Cannabinus*	36	21	18	2	5
Ramie	*Boehmeria nivea Gaud*, variety *tenacissima*	68.6-76	13.1-15.0	0.6-1	1.9-2	6
Hemp	*Cannabis sativa* L.	70-78	17.9-22	3.7-5	0.9	7
Cotton	*Gossypium* spp.(*commonest G. hirsutum*)	82.7-92	2-5.7	0.5-1	5.7	8
Coir	*Cocos nucifera* L.	43	0.3	45	4.0	9
Banana	*Musa acuminata* L.	60-65	6-19	5-10	3-5	10
Henequén	*Agava fourcroydes Lemaire*	60-78	4-28	8-13	3-4	5
Bagasse	*Saccharum officinarum* L.	40	30	20	10	5
Pineapple	*Acanas Comosus*	80-81	16-19	12	2-2.5	11
Wood	-	45-50	23	27	-	11

*1. (Gassan, Chate and Bledzki 2001; Smeder and Liljedahl 1996; Bledski and Gassan 1999; Bledski, Reihmana and Gassan 1996 ; Mwaikambo and Ansell 2002).
2. (Gassan, Chate and Bledzki 2001; Smeder and Liljedahl 1996; Bledski and Gassan 1999; Bledski, Reihmana and Gassan 1996).
3. (RunCang Sun et al. 1998; Rowell et al. 1997).
4. (Joseph et al. 2002; Bledski and Gassan 1999; Rowell et al. 1997; Bledski, Reihmana and Gassan 1996; Mwaikambo and Ansell 2002).
5. (Klemm, Schmauder and Heinze 2001).
6,. (Bledski and Gassan 1999; Bledski, Reihmana and Gassan 1996; Mwaikambo and Ansell 2002).
7. (Bledski, Reihmana and Gassan 1996).
8. (Smeder and Liljedahl 1996; Bledski and Gassan 1999; Mwaikambo and Ansell 2002; Klemm, Schmauder and Heinze 2001).
9. (Gassan, Chate and Bledzki 2001; Bledski, Reihmana and Gassan 1996).
10. (Gassan, Chate and Bledzki 2001; Smeder and Liljedahl 1996)
11. (Gassan, Chate and Bledzki 2001).

usually consist of over 500,000 cellulose molecules. So, if a fibre consists of 500,000 cellulose molecules with 5,000 glucose resides/cellulose molecules, the fibre would contain about 2.5 billion H-bonds. Even if a H-bond has about 1/10 the strength of a covalent bond, the cumulative bonding energy of 2.5 billion of them is awesome. It is the H-bonding that forms the basis for the high tensile strength of cellulose.

Cellulose I is the most common crystalline form (allomorph) of native cellulose. Cellulose I is metastable and can be irreversibly converted into another crystalline state, cellulose II, the most stable allomorph known (Ranby 1952) differing from cellulose I in unit cell dimensions and, possibly, in chain polarity (see Table B). Cellulose I has parallel glucan chains and strong intramolecular hydrogen bonds. In nature, cellulose I exist as two crystalline sub-allomorphs, cellulose I-α and cellulose I-β (Atalla and Vanderhart 1984). Cellulose II is seldom found naturally and is generally the product of re-precipitation after swelling and dissolution of cellulose I with various solvents. It is more commonly known as “Rayon” (Roberts, Saxena and Brown 1989) ?The glucan chains of cellulose II are anti-parallel, probably as a result of chain folding (Kuga, Takagi and Brown 1993). Other allomorphs of cellulose such as cellulose III and IV are known but seldom, if ever, occur in nature. Meyer, Mark, and Misch (Meyer and Mark 1928; Meyer and Misch 1937) proposed a unit cell of the crystal lattice, already 60 years ago, that is still applica-

FIGURE 3. Haworth projection formula of cellulose. (Nevell and Zeronian 1985).

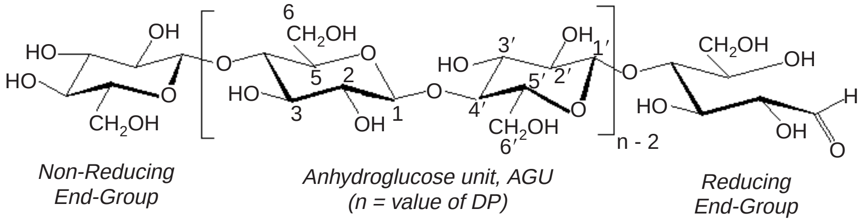


TABLE B. Unit cell dimensions of various cellulose allomorphs (Krassig, 1993).

Polymorph	**a-axis (Å)**	**b-axis (Å)**	**c-axis (Å)**	**γ-axis (Å)**
Cellulose I	7.85	8.17	10.34	96.4
Cellulose II	9.08	7.92	10.34	117.3
Cellulose III	7.74	7.74	10.30	122
Cellulose IV	8.11	8.11	10.30	90

ble for practical purposes today (Figure 4). The dimensions of the cell are reported in Table B.

Hemicellulose

A fourth form of sugar polymers found in biomass is hemicellulose. Hemicellulose consists of short, highly branched chains of sugars (Figure 5). It contains five-carbon sugars (usually D-xylose and L-arabinose), six-carbon sugars (D-galactose, D-glucose and D-mannose) and uronic acid. The sugars are highly substituted with acetic acid. Its branched nature renders hemicellulose amorphous and relatively easy to hydrolyse to its constituent. When hydrolysed, the hemicellulose from hardwood releases products high in xylose (a five-carbon sugar). The hemicellulose contained in softwood, in contrast, yields more six-carbon sugars. In contrast to cellulose that is crystalline, strong and

FIGURE 4. Unit cell of cellulose I according to the Meyer-Misch model.

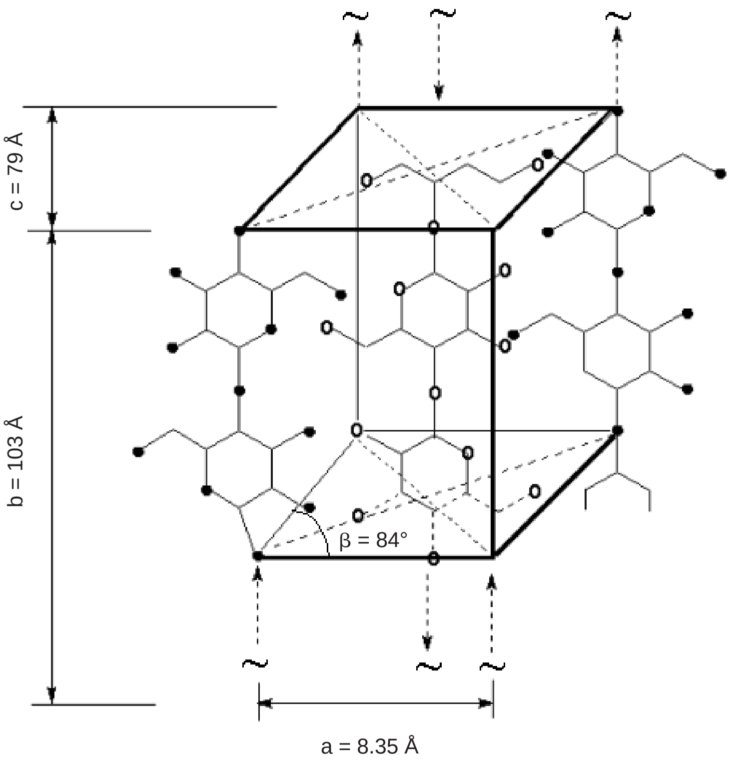
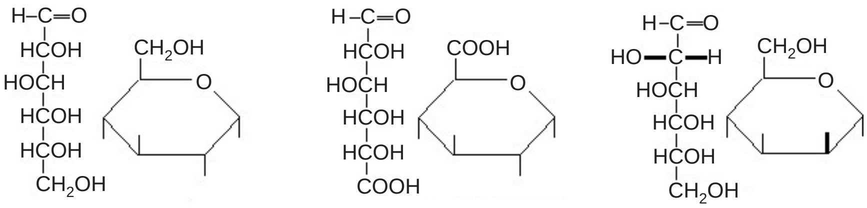
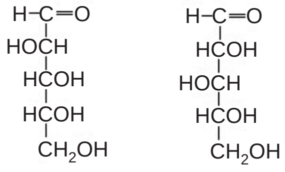


FIGURE 5. Some monomers of hemicellulose.



D - glucose D - glucuronic acid D - mannose



D - arabinose D - xylose

resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolysed by dilute acid or base, but nature provides an arsenal of hemicellulase enzymes for its hydrolysis. These enzymes are commercially important because they open the structure of wood for easier bleaching leading to the substitution of older methods of bleaching that consume larger amounts of chemicals dangerous for the environment, such as chlorine (Kuhad, Singh and Ericksson 1997).

All of the changes in the fibres dimensions with changing environmental conditions can be attributed to hemicellulose swelling with adsorbed water. Small ions like lithium and sodium can join and stabilise adsorbed water molecules (the effects of sodium ions is more significant at low moisture contents as they can raise the equilibrium moisture content by up to 2%). In dry conditions, hemicellulose breaks down into carbon dioxide and water. At 20°C, this degradation can already reduce wood weight by 1%. Under wet conditions, acid hydrolysis accelerates the hemicellulose degradation into mostly sugar molecules. Obviously, these degradation processes are faster at higher temperatures (Stamm 1971).

Lignin

Lignin is formed by the removal of water from sugar to create aromatic structures. These reactions are not reversible. There are many possible monomers of lignin and the types and proportions depend on the source in nature. Some typical monomers are shown in Figure 6a and an early stage in the condensation process of these monomers to form lignin is shown in Figure 6b. In this last figure several chemical groups that may react further are highlighted. Large lignin molecules are three-dimensional and are heavily cross-linked. Sometimes lignin is isolated as a brown powder, but more often it is a gummy mixture of lignins with a wide range of molecular weights. Lignin resists attack by most microorganisms and anaerobic processes tend not to attack the aromatic rings at all. The aerobic breakdown of lignin is slow and may take months. Lignin together with hemicellulose is nature's cement in the exploitation of the strength of cellulose while conferring flexibility.

Physical Structure

Physically, vegetable fibres are a collection of long, thin, pointed cells made up of cell walls on the outside and air on the inside. A simplified scheme of the cell wall is shown in Figure 7a-b. Each cell wall has four layers, with the "primary" layer on the outside and three "secondary" layers inside. The amount of hemicellulose is about the same in each layer because the layers need to swell and contract together without stress between them when the moisture content changes. The cellulose content of each layer increases steadily from the outer "primary" layer to the innermost "secondary" layer. The lignin content consequently decreases in that sequence. The cellulose microfibrils lie parallel to each other within each layer and spiral around the cell's long direction. Different layers have different angles of spiralling. The hemicellulose combined with the lignin acts as glue that holds the layers together and the cellulose microfibrils within each layer. Most cells have their long directions parallel to the direction of plant growth. The wall of each cell has a cross-sectional shape that is rectangular with slightly rounded corners. Adjacent cells have their walls glued to one-another by a mixture of about three-quarters lignin and a quarter hemicellulose. The glue layer is about as thick as an individual cell-wall layer except at the rounded corners, where it fills the space. Pairs of glued-together adjacent cell walls act as structural units. There are evenly-spaced holes in the cell walls called "pits" which usually line up with similar holes in adjacent cell walls. These holes allow the passage of water or air between the cells and ultimately between the inside and outside of the fibre.

So, vegetable fibres can be considered as advanced composite materials themselves with a taylor made distribution of structural cellulose fibres in a functional hemicellulose-lignin matrix that has also taylor-made mechanical and diffusion control properties.

FIGURE 6. Some typical monomers of the lignin (a) and early stage in their condensation (b).

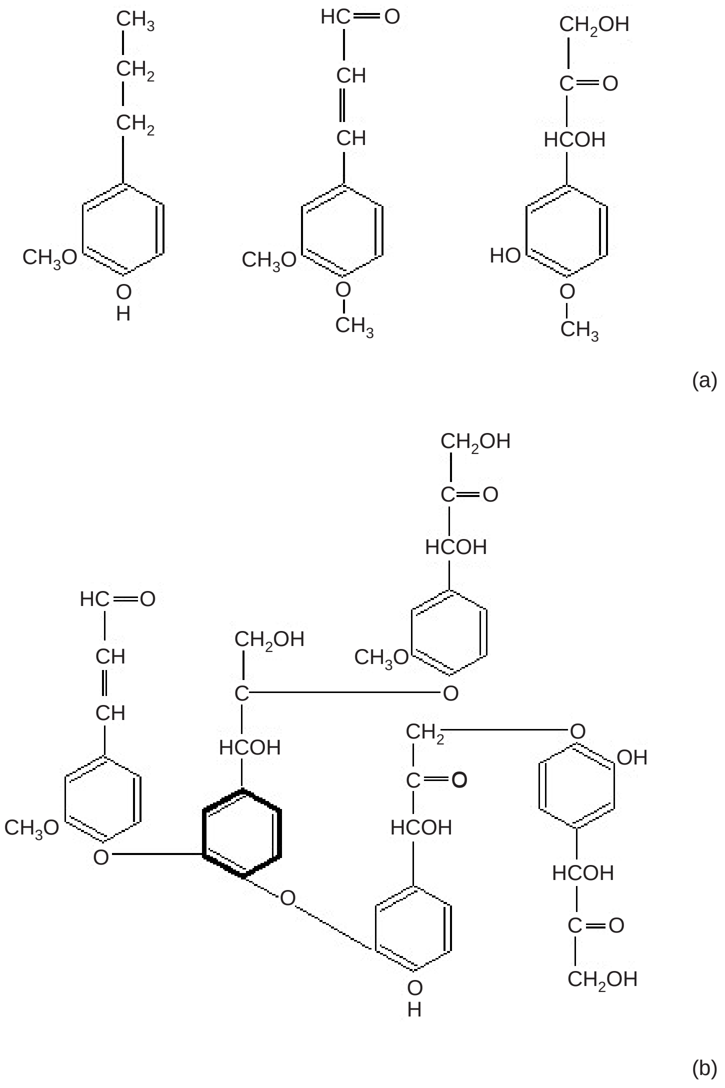
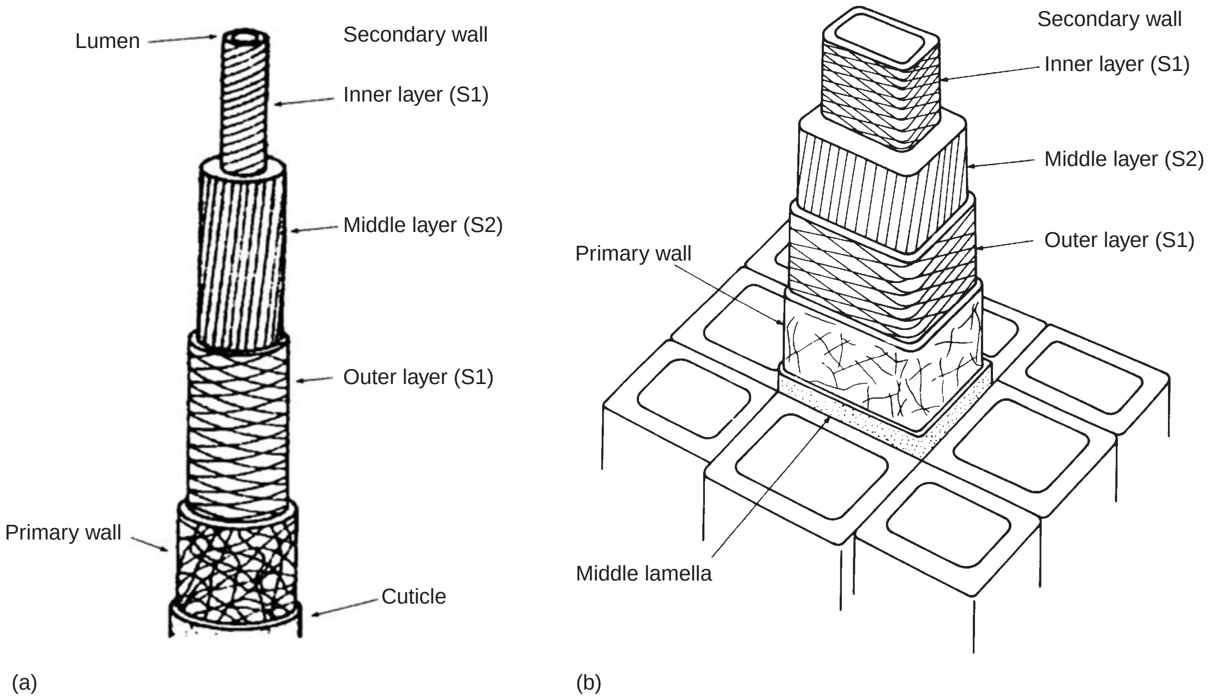


FIGURE 7. Scheme of the morphological architecture of a cotton fibre (a) and a delignified spruce wood (b).



Fibre Production

After the planting and growing phase, which takes about one year, depending on the variety of the plant and the final desired quality, the fibres are harvested. In general, the harvesting should tend to preserve the maximum final length of the fibre. In fact, as in the case of their application as composite reinforcements, the greater the aspect ratio (length/diameter) of the fibre, the better the improvement of the final mechanical properties.

A simple process, named decortication, is also normally used to extract leaf fibres. Leaves are crushed and beaten by a rotating wheel set with blunt knives, so that only the fibres remain. All the other parts of the leaf are washed away by water. Decorticated fibres are then washed before drying them in the sun or with hot air. The dry fibres are machine combed and sorted into various grades, largely on the basis of the previous in-field separation of leaves into size groups (Yayock, Lombin and Owonubi, 1988).

The extraction of bast fibres from the stems of the plant-fibres is in general accomplished through retting processes, described hereunder.

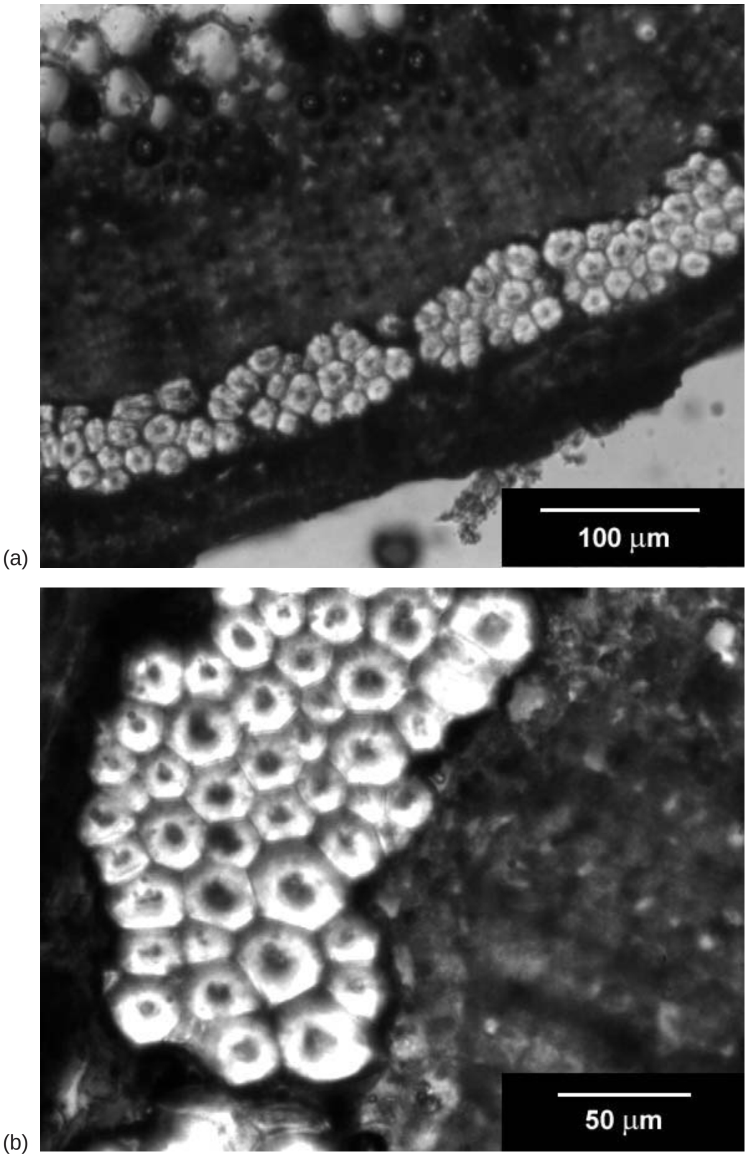
Retting

Retting is a microbial process that breaks the chemical bonds that hold the stem together and allows separation of the bast fibres from the woody core. The two traditional types of retting are field retting and water retting. With field or dew retting, plant stems are cut or pulled up and left in the field to rot. Farmers monitor the process closely to ensure that the bast fibres separate from the inner core without much deterioration in quality. Moisture is needed for the microbial breakdown to occur, but then the weather must be dry enough for the stalks to dry for bailing. Although varying weather conditions affect the quality of the fibre, field retting has been used extensively because it is inexpensive, mechanized and does not use water. Currently, dew-retting, which depends on indigenous, aerobic fungi to colonize pulled plants in the fields, is the accepted practice in European countries and accounts for much of the fibres used in textiles. However, the disadvantages of dew retting include: (1) the dependence on particular geographical regions that have the appropriate moisture and temperature ranges for retting, (2) coarser and lower quality fibres than those produced with water-retting, (3) less consistency in fibre characteristics and (4) the occupation of agricultural fields for several weeks (Van Sumere 1992). Dew-retting further results in a heavily contaminated fibre that is particularly disadvantageous in cotton textile mills. On the other hand, water retting produces more uniform and high-quality fibre but the process is very labour and capital intensive. In this case, stems are immersed in water (rivers, ponds or tanks) and monitored frequently. Not only is this labour intensive, but farmers and/or workers must also have the necessary knowledge regarding fibre quality. Furthermore, the process uses large volumes of clean water that must be treated before being discharged. Water retting, which was formerly the method of choice because of high quality fibre, produces environmentally unacceptable fermentation waste (Sharma and Van Sumere, 1992a; Sharma and Van Sumere, 1992b). This practice was mostly discontinued in western countries several decades ago because of the pollution from fermentation products and the high cost of drying (Brown, 1984).

An alternative that has had long-term consideration is the use of enzymes in controlled reactors. Scientists speculate that improved microorganisms or direct use of enzymes may allow countries in Europe and North America to produce textile-quality bast fibres. The cost of the enzymes, and perhaps other less obvious reasons, have prevented a further development of a commercial enzyme-retting process and dew-retting remains the most widely used practice in Europe to obtain fibres commercially for industrial use, despite continuing research on other methods. In this scenery, the work performed by the Finnish factory Finflax, as a partner of the European Project ECOFINA (Ecoefficient Technologies and Products based on Natural Fibre Composites) as a provider of flax fibre can be mentioned as they uses a controlled enzymatic retting of flax fibre to obtain a higher quality fibre for composite materials (Kenny 2003). In this process, the anatomy of the fibres and fibre bundles determines on a large extent the final fibre quality and yield and it is also dependent on the flax cultivation and growth conditions within the stem. The quality of the fibres is also largely determined by the shape of the bundles; oval or kidney-shaped fibre bundles being characteristics of good quality flax, while irregular bundles are indicative of poor quality flax. Furthermore, both fibre yield and quality are strongly dependent on the characteristics of the cell walls, for example, better fibre quality and higher yields correspond with thicker cell walls, while fibre strength is mainly determined by the cell shape and the characteristics of the middle lamellae.

In order to achieve good quality fibre, it is important to focus on all the steps in the refining process. The selection of flax, to be retted industrially, must start already at beginning of the production of the raw material, in particular microbiological and microscopical (light and electron microscopy) examinations should be taken into account. Microbiological tests are performed using standard plate culture methods in order to investigate the quality of the fibre. This was examined with an optical microscope (Figures 8a-b). A well formed fibre bundle, oval cross section form of fibres and well packed fibre cells are signs of good quality fibres. The number of fibre bundles vary from stem to stem and depend on which part of the stem is used. For example, bundles are less numerous at the top of the plant than at the root, while most bundles are found in the middle part of the stem. The number of fibre bundles varies from 15 to 35. A fibre bundle usually contains from 10 to 40 fibre cells

FIGURE 8. Before retting cross-section, of (a) portion of the flax stem and (b) flax fibre bundle with surrounding tissue.



having a diameter of 20 to 30 µm. The amount of fibre cells differ from bundle to bundle, the largest amount being found in the middle part of the stem. The primary wall of the flax fibre cell contains pectic substances, occasionally with traces of lignin, whereas the secondary layers consist mainly of cellulose. The retting time may easily vary (12-24 hours) depending on the enzyme concentration, the type of fibres to be retted and the final quality of fibres required for different technical applications. Figures 9a-b show the quality of the flax fibres retted enzymatically by the Arctic-Flax Process used by Finflax. The enzymes break the pectin substances of the flax fibre cell walls. The retting time is over 22 hours, because the aim is to break off the fibre bundle and produce elementary fibres.

Fibre Separation

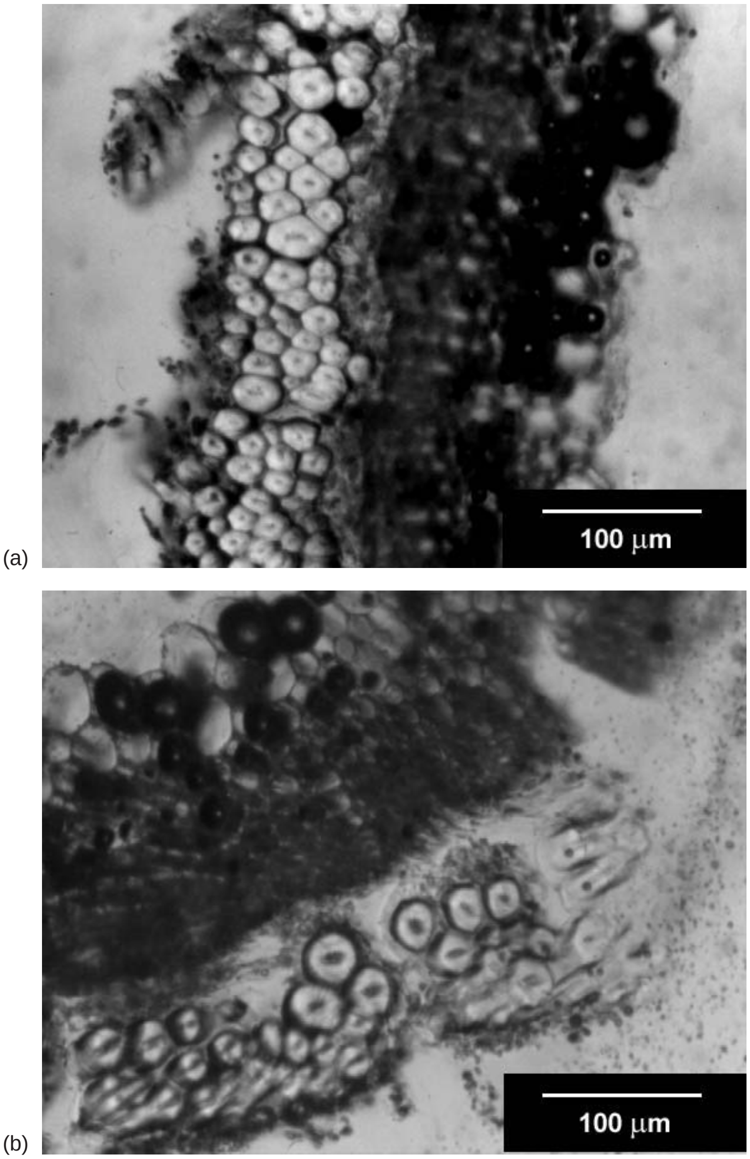
Once the stalks are retted, dried and baled, they are processed by mechanical separation, in a process called scutching that include two operations: breaking and swingling. In the breaking, stalks are passed between fluted rollers to crush and break the woody core into short pieces of less than 1 cm length, called shives. Swingling is the removal of the shives and is achieved by tangential scraping of the broken stems. The process of long fibre scutching produces two kinds of fibres, scutched flax (long fibre) and tow (short fibre). Although partially mechanized, these procedures are functionally identical to traditional methods by hand of preparing line fibre and tow for twisting into twine or rope or for spinning into yarn. Not only are these methods time consuming but they also require skilled workers and a considerable investment in capital equipment.

It is also possible to mechanically convert virtually all of the bast fibre directly into tow using flax breaking and tow processing machinery. This eliminates traditional scutching and allows the processing of randomly-oriented baled straw. Compared to scutching machinery, tow-processing equipment usually has a higher throughput, requires fewer and less skilled workers and costs less. However, a tow processing system cuts all of the bast fibre into short lengths, making it appropriate only for lower value uses, such as pulp and paper, instead of textiles or composites.

Hackling

This is the final process before spinning. It is the removal of all bits of fibre straw and all short fibres (tow). There are three to four sets of hackles, starting with the very coarse set and continuing on to the very fine toothed set. The fibres are flicked over the coarsest hackle first until no coarse fibres can be removed from the fibres held in hand. This process is repeated with the second coarsest hackle, using only the fibre remaining in the hand. Flicking and draw-

FIGURE 9. The end-point of the enzymatic retting (a), followed by the breaking of pectic substances of the flax fibre cell (b).



ing continues through the various hackles until the fibre remaining in the hand is of a smooth and consistent length.

The fibre remaining in the hand is called a line, strick, hank or lint. The fibre remaining in the hackles is removed and the hackling process is repeated. This fibre is called tow and is used for sacking, candle wicks, tow ropes and other similar coarse materials. The straw remaining is used in bedding and is considered to repel fleas and lice.

Spinning, Weaving and Finishing

In spinning, the fine fibres are twisted together to obtain a yarn. Finer yarns are generally spun with water (wet spun) and the coarser yarns are dry spun. The weaver will generally use wet spun yarns for nicer apparel and household fabrics and dry spun (tow) for coarser upholstery items. The basic principles of weaving have not changed since linen was first invented. However, technology has changed considerably over the centuries, and today weaving is a very sophisticated operation. The non-wovens were manufactured by a full-scale scutching, opening, carding and needle-punch process. The technological parameters have an extended influence on the fabric and the later composite properties; needle penetration and stitch density in needling can change the tensile strength, the flexing resistance and the E-modulus. The objective of carding is to open the processed fibre without damaging its technical properties. The carding functions are:

- opening the fibre bundles into single fibres and cleaning of the fibres
- unidirectionaling and straightening of the fibres
- removal of very short fibres

The fibres can be processed with the non-woven carding process. After carding, the fibres can be also processed into different square-weighted mats by needle-punching.

Steam Explosion

Research in Europe has sought methods for separating bast fibre that bypass traditional retting and scutching. Steam explosion and ultrasound are under investigation in Germany, but the processes produce short fibres only (D’Agostino, Richard and Taylor 1996; Kessler et al. 1998). In the early 1930’s, Charles V. Rowell published a patent, which used the technique of steam explosion to extract fibres from agricultural wastes (Rowell 1932). In the 1970’s and 1980’s, several commercial and academic organizations began conducting research and development that explored other applications for steam explosion, including the production of cattle-feed, ethanol and specialty chemicals from wood fibres. Certain heat transfer limitations which hinder process optimisation are associated with batch steam explosion. In 1986, an experimental station that uses steam explosion (STEX) started in Germany to produce short staple linen fibres and can be processed on a highly productive cotton line in mixtures. The processing of flax by STEX can be adjusted to variable raw material quality and provides short fibres of high purity and free-ness due to a chemical treatment during steaming and a mechanical action when the material is expelled from the reaction chamber.

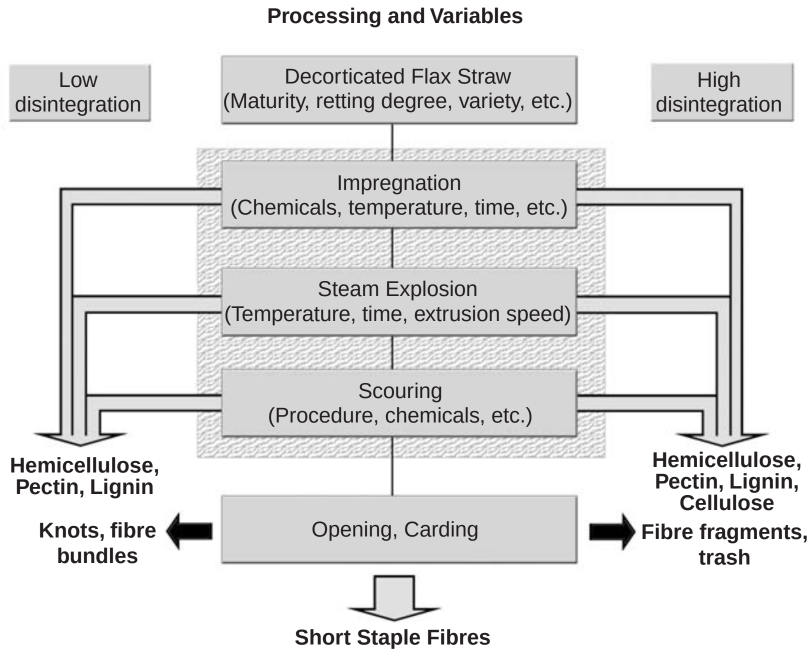
Steam explosion generally refers to the process of exposing fibres to high-pressure steam (typically 200-450 psi) for a period of 1-10 minutes and then explosively discharging the product to atmospheric pressure. The process has, in the past, been mistakenly described as a physical treatment. However, it is now well accepted that the process is chemical in nature and is controlled by temperature and time. In order to utilize the fibres, it is necessary to separate the lignin from the cellulose. In the past, it was only possible to break the bonding between the cellulose and the lignin through very expensive and high polluting chemical pulping processes. Continuous steam explosion pulping uses high-pressure steam, under controlled conditions of time and temperature, to alter the natural structure of lignocellulosic materials and achieves significant reductions in chemical requirements and refining energy. The strength characteristics of the resulting pulps are improved and respond well to bleaching with hydrogen peroxide. In Figure 10, a schematic diagram of the steam explosion treatment of decorticated flax fibre is shown (Kessler et al. 1998). The decorticated fibre bundles are impregnated with NaOH at a concentration range of 0.1-0.5% wt at different temperatures (20-120°C) in the reaction chamber. After releasing the surplus base, the material is subjected to saturated steam. According to the specified steam treatment, the material is extruded into a cyclone by suddenly opening the extrusion valve at the defined release pressure. The degraded materials, like pectin and hemicellulose are then extracted by alkaline scouring. Following the wash cycle, the fibres are dried at room temperature, opened on a standard opener and carded.

In conclusion, natural fibres processed by steam explosion offer the opportunity for high-tech applications in textiles as well as in technical applications which may balance farming and productions costs, for its better spinnability in comparison to mechanically cottonized flax, due to a higher degree of freeness, homogeneity and purity.

Thermal Properties

Main thermal properties of vegetable fibres for composite materials are thermal expansion and thermal degradation. In spite of other clear advantages, the thermal properties of vegetable fibres represent a clear drawback in com-

FIGURE 10. Schematic representation of the flax steam explosion treatment.



parison with synthetic fibres. Regarding thermal expansion only few data are available in the scientific literature with values of the corresponding coefficient ranging in the order of $3 \cdot 10^{-5}$, while glass fibres are in the order of $5 \cdot 10^{-6}$. On the other hand, thermogravimetric and differential scanning calorimetric analysis demonstrate that noticeable mass loss in natural fibres start at about 200-220°C; above this temperature irreversible degradation of the fibres occurs (Wielage et al. 1999). The relative low degradation temperatures of vegetable reinforcements, in comparison with the process temperatures of polymeric matrices, represents the most important limit for their use in plastics with the conventional processing equipments (extruder, injection moulding, etc). However, the thermal stability of the cellulose-based fibres can be improved with several physical and chemical treatments as described in the second part of this work. Therefore, an intense research activity on the thermal degradation of vegetable fibres for composites has been reported in the scientific literature. Only some results, related to the effects of chemical treatments on the thermal stability of natural fibres are reported here as examples. Rana et al. investigated the thermal behaviour of untreated and acetylated jute fibres, characterizing the hemicellulose and α-cellulose decomposition temperatures (found also in DSC tests) and showing the missing of the first peak and the increase of the second peak temperature for treated fibres, due to higher thermal stability (Rana et al. 1997). Albano et al. studied the effect of acetylated and non-acetylated sisal fibres on the thermal degradation of blends of PP and polyolefins, especially PP/HDPE/functionalized EPR and PP/HDPE/non-functionalized EPR (Albano et al. 1999). The studies have shown that the starting temperature of the decomposition of the fibre, whether treated or not, was maintained almost at the same level and acetylated fibre stability was also found to increase with a higher activation energy value (for acetylated fibre). A change in the degradation mechanisms with two stages degradation for the treated fibres was also observed.

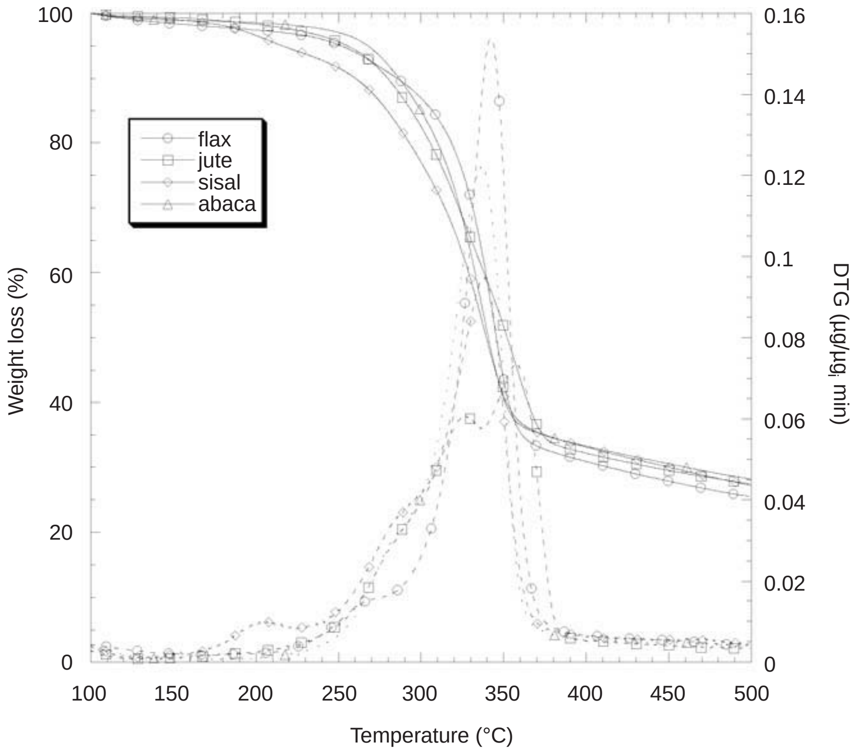
Thermogravimetric analysis, TGA, of untreated and different surface modified jute fibres was also performed by Mohanty et al. (Mohanty, Khan and Hinrichsen 2000) for the realization of composites based on a Biopol matrix; all surface modified fabrics show the same or better thermal stability compared to untreated fabrics. Typical TGA curves of some untreated vegetable fibres are illustrate in Figure 11. In any case processing and service temperatures for vegetable fibres cannot exceed 200-200°C limiting the availability of suitable polymeric matrix. These aspects will be specifically addressed in the second part of this review.

Although many research reports indicate that natural fibres exhibit a complicated anisotropic structure, unfortunately the anisotropy property of most natural fibres has been left undetermined. For example, the jute fibres investigated by Cichocki and Thomason exhibited considerable elastic and thermal expansion anisotropy (Cichocki and Thomason 2002). The longitudinal Young's modulus of the fibre was determined to exceed the transverse fibre modulus by as much as an order of magnitude in certain temperature regimes. The fibres exhibited negative thermal expansion coefficients along their lengths; however, large positive thermal expansion coefficients, similar in magnitude to many polymeric materials, have been estimated in the transverse directions.

Mechanical Properties

The properties of the fibres are determined by the physical, mechanical and chemical properties of the morphological constituents and their interfaces. Main physical characteristics found in literature regarding the most widely known natural fibres are reported in Table C. Natural fibre consists of highly crystalline cellulose fibrils spirally wound in a matrix of amorphous hemicellulose, lignin and, eventually, pectin. Lignin and pectin act mainly as bonding agents. The characteristic values of the structural parameters vary from one fibre to another. In the case of flax fibre, they are oriented with a tilt angle of 10° to the axis of the fibre and hence display a unidirectional structure (Bos

FIGURE 11. Typical thermogravimetric curves for some natural fibres.



and Donald 1999). In a recent research the Young's modulus of a flax fibre was estimated by taking into account the composition of the fibre and the evolution of the orientation of the fibrils during a tensile test, using micro-mechanical equations well compared with experimental results (Baley 2002).

The calculation of the elastic properties of cellulose based natural fibres was performed by Gassan et al. (Gassan, Chate and Bledzki 2001) by means of different mechanical models. The results shown how the modulus in fibre axis decreases with an increasing spiral angle and degree of anisotropy, while shear modulus reached a maximum value at a spiral angle of 45°. Moreover, the degree of anisotropy was only affected by the cellulose content in the range between 35 and 90%, which is the typical content for most natural fibres.

Eichhorn et al. (Eichhorn, Sirichaist and Young 2001) utilized Raman spectroscopy in order to probe the deformation mechanism of cellulose fibres. During tensile deformation, the 1095 cm^{-1} Raman band, corresponding to the

TABLE C. Main physical properties of cellulose based fibres compared with conventional synthetic fibres.

Fiber	**Density** (g/cm^3)	**Diameter** (µm)	**Elongation at break** (%)	**Tensile strength** (MPa)	**Young's Modulus** (GPa)	**Specific modulus** (GPa·cm^3/g)	**Price** (€/Kg)	**References***
Flax	1.40-1.50	40-620	2.7-3.2	343-1035	27-80	19-53	2.29-11.47	1
Jute	1.30-1.50	30-140	1.4-3.1	187-773	3-55	2-37	0.12-0.35	1
Abaca	1.50	17-21	10-12	980	72	48	0.81-0.92	2
Sisal	1.30-1.50	100-300	2.0-2.9	507-855	9.0-28.0	7-19	0.70-1.02	3
Kenaf	1.22-1.40	40-90	3.7-6.9	295-930	22-53	18-38	0.53-0.61	2
Ramie	1.50	40-60	3.6-3.8	400-938	44-128	29-85	1.44-2.40	4
Hemp	1.40-1.50	16-50	1.3-4.7	580-1110	3-90	2-60	0.57-1.73	5
Cotton	1.50-1.60	16-21	2.0-10.0	287-597	5.5-12.6	4-8	1.61-4.59	6
Coir	1.25-1.50	100-450	15.0-47.0	106-270	3.0-6.0	2-4	0.24-0.48	7
Banana	1.30-1.35	50-280	3-10	529-914	7.7-32.0	6-24	0.7-0.9	8
Henequén	1.49	20-500	3.0-5.0	430-580	10.1-16.3	7-11	0.38-0.67	8
Bagasse	0.55-1.25	200-400	0.9	20-290	2.7-17.0	5-14	0.15	9
Pineapple	1.52-1.56	200-8800	0.8-3.0	170-1627	6.21-82	4-53	0.36-0.72	10
E-glass	2.50-2.55	10-20	2.5	2000-3500	73.0	29	1.25	11
Aramide	1.40-1.45	12	3.3-3.7	3000-3150	63.0-67.0	45-48	7.20	11
Carbon	1.40-1.75	5.5-6.9	1.4-1.8	4000	230.0-240.0	164-171	12.0	11

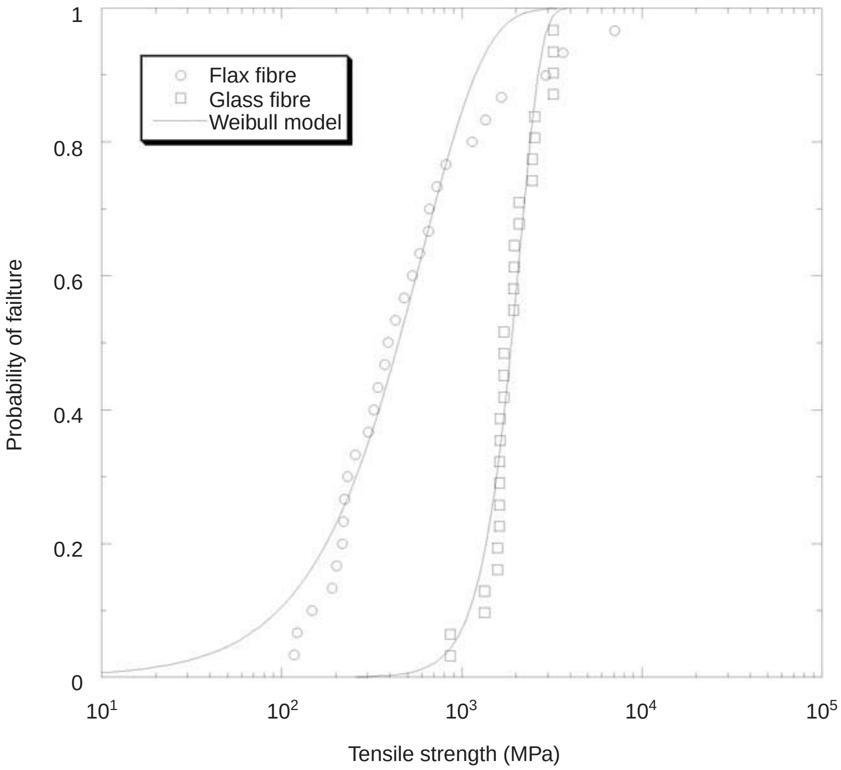
*1. (Gassan and Bledzki 1999; Van Rijswijk and Brouwer 2002).
2. (Karus, Kaup and Lohmeyer 2000).
3. (Gassan and Bledzki 1999; Kalaprasad, Joseph and Thomas 1997; Nabi Saheb and Jog 1999).
4. (Gassan and Bledzki 1999; Van Rijswijk and Brouwer 2002; Vázquez and Domínguez 1999).
5. (Van Rijswijk and Brouwer 2002).
6. (Gassan and Bledzki 1999; Baley, D'Anselme and Guyader 1997).
7. (Van Rijswijk and Brouwer 2002; Baley, D'Anselme and Guyader 1997; Geethemma et al. 1998).
8. (Baley, D'Anselme and Guyader 1997).
9. (Vázquez, Domínguez and Kenny, 1999).
10. (Nabi Saheb and Jog 1999; Uma Devi, Bhagawan and Thomas 1997; Satyanarayana et al. 1990; Geethemma et al. 1998).
11. (Saechtling 1987).

stretching of the cellulose ring structure, shifted towards a lower wavenumber due to molecular deformation.

In contrast with more uniform synthetic fibres, whose properties can be easily and univocally determined, natural fibres are characterized by a large dispersion of their characteristics, as evidenced in Figure 12. Tensile properties of natural fibres exhibit considerable scatter thus requiring statistical analysis (Bledski and Gassan 1999; Biagiotti et al. 2003). The two-parameter Weibull distribution (Weibull 1951), which expresses the cumulative density function of the studied property of the fibres as:

$$F\left(E_f\right) = 1 - \exp\left[-\left(\frac{E_f}{E_0}\right)^a\right] \tag{1}$$

FIGURE 12. Comparison between Weibull distributions of flax and glass fibres. (Biagiotti et al. 2003).



where a is a dimensionless shape parameter and E_0 is a location parameter, is found to provide good agreement with the natural fibres tensile data (elastic modulus and tensile strength) (Van de Weyenberg, Ivens and Verpoest 2000). However, for a more accurate modelling the three-parameter Weibull model is some times adopted (Kompella and Lambros 2002; Joffe, Andersons and Wallstrom 2002). Such features make it necessary to utilize a more systematic statistical approach to define their properties and those of their relative composites (Hu and Hsieh 1997). In order to describe the mechanical characteristics of natural fibres, a preliminary study was conducted using statistical representations based on the probability density functions of the quantities of interest (Biagiotti et al. 2003). The variation of the elastic modulus and the tensile strength of the natural fibres with the diameter size were predicted in a first approach, by means of the model proposed by Griffith (Griffith 1921). Then, the statistical approach presented utilized the distribution of the geometric properties of the measured fibres, over a post-processed composite, to obtain a statistical distribution of the mechanical response of the composite through the non-linear equations arising from the combination of mechanical models. The true distribution functions were explicitly estimated with the help of semi-parametric algorithms, drawn from the neural network literature.

Influence of Environmental Conditions on Fibre Properties

It is well established that natural fibres are susceptible to moisture (McKenzie 1979; Maldas and Kokta 1989). Cellulose, which is the main constituent of the cell wall of natural reinforcements, in fact, contains numerous hydroxyl groups that are strongly hydrophilic. The moisture content of natural fibre is also a function of the fraction of non-crystalline regions and of void content (Bledzki and Gassan 1999). Therefore, natural fibre-reinforced composites can absorb a great amount of water, which generally causes a reduction in their mechanical properties (Karmaker 1994). Generally, the water content in these systems is about 10-20 %wt. under standard conditions. The rate of water absorption in a composite depends on many factors: the kind of fibre and matrix, temperature conditions, differences in water distribution within the composite, reaction between water and the matrix and others variables (Wolff 1993). Both the rate of water pick-up and the total amount of moisture absorbed depend on the chemical structure of the resin and crosslinking agent together with the temperature and relative humidity. The moisture absorbed not only plasticizes the matrix resin, but also changes the state of stress in favour of cracking through swelling (Pritchard and Speake 1987). Moisture effects in fibre-reinforced plastic composites have been studied extensively during the lasts two decades (Mahlberg et al. 2001). This drawback represents one of the major restrictions of natural fibre in durable composite applications for the consequent poor dimensional stability (swelling) and their susceptibility to rotting (Peijs et al. 1998). Swelling of fibres can lead to microcracking of the composite and degradation of the mechanical properties. Moreover, the processing of thermoplastic matrix based composites and the moisture content can lead to poor processability and porous products due to the evaporation of water during the conventional thermal steps of the process. At the fibre/matrix interface, moisture may reduce the bond strength by breaking the bonds (Chua, Dai and Piggot 1992).

Other environmental factors, such as solvents, oil and radiation can also influence the properties of natural materials during their service-life (George, Bhagawan and Thomas 1998). At lower temperatures, the translational freedom of water molecules is slowly hindered by the stiffness of polymer chain segments. Moisture diffuses into a polymer to varying degrees depending on molecular and microstructural aspects such as polarity, the extent of crystallinity of thermoplastics and the presence of residual hardeners or other water-attracting species (Jones 1994). In the absence of radiation, the environmental degradation of the mechanical properties of polymers is generally associated with plasticization, weight loss, micro-mechanical damage and blistering, induced by the sorbed solvents. Loss of material by leaching after longer time periods also leads to effective damage.

The moisture absorption of fibres can be minimized in the composite by encapsulation by the polymer and good fibre-matrix adhesion. Good adhesion can also reduce the rate and amount of water absorbed in the interphase region of the composite. It is difficult to entirely eliminate the absorption of moisture without using expensive surface barriers on the composite surface (Rowell et al. 1999). The moisture resistance of natural fibres can, however, be improved through fibre treatments like acetylation and a novel upgrading process based on three steps: hydro-thermolysis, drying and curing of flax fibre (Stamboulis, Baillie and Peijs 2001).

CONCLUSIONS

The recent environment-conservative regulations have motivated new efforts in research and development of new products and processes reducing further dependency on oil reserves. The possibility to use natural fibres as reinforcements for composite materials offers an adequate reply to these considerations. The lower specific gravity of the cellulosic-based fibers (approximately 1.4 g/cm^3 as compared to about 2.5 g/cm^3 for mineral based systems) leads to weight savings in composite structures with direct implications in transport applications. Moreover, their specific mechanical properties appear to be competitive to the other conventional fibres. Costs of natural fibres are, in general, close or lower than plastic and high fibre loading can result in significant material cost savings. Other advantages can be found in their non-abrasive nature. In fact, reduced equipments abrasion and the subsequent reduction of re-tooling costs through the use of natural fibres is a factor that will be considered by the plastics industry when evaluating the use natural fibres.

On the other hand, despite the numerous advantages that vegetable fibres present in a first approach, the series of drawbacks discussed in previous paragraphs (scattered mechanical properties, low process temperatures, easy moisture absorption, etc) can limit their utilisation in industrial scale. Then, although extensive research efforts have been dedicated to the production of industrial vegetable fibres suitable for composite materials several aspects still require attention before this industrial sector can be considered as mature.

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